DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The figure which illustrates a thermoelectric element theoretically
[Drawing 2]The figure showing the example of a mode of a thermoelectric element
[Drawing 3]The figure showing the example of the thermoelectrical characteristic from the low temperature of n type oxide thermoelectrical conversion material to an elevated temperature
[Drawing 4]The figure showing the example of the thermoelectrical characteristic from the ordinary temperature of n type oxide thermoelectrical conversion material to an elevated temperature
[Drawing 5]The figure showing the example of the thermoelectrical characteristic from the ordinary temperature of n type oxide thermoelectrical conversion material to an elevated temperature
[Drawing 6]The figure showing the example of the thermoelectrical characteristic from the low temperature of p type oxide thermoelectrical conversion material to an elevated temperature
[Drawing 7]The figure showing the example of the thermoelectrical characteristic from the ordinary temperature of p type oxide thermoelectrical conversion material to an elevated temperature
[Drawing 8]The figure showing Example 1
[Drawing 9]The figure showing Example 1
[Drawing 10]The figure showing Example 1
[Drawing 11]The figure showing Example 2
[Drawing 12]The figure showing Example 2
[Drawing 13]The figure showing Example 3
[Drawing 14]The figure showing Example 3
[Drawing 15]The figure showing Example 3
[Drawing 16]The figure showing Example 4

[Drawing 17]The figure showing Example 5
[Drawing 18]The figure showing Example 6
[Drawing 19]The figure showing Example 7

[Description of Notations]

1 P-type semiconductor (p type thermoelectrical conversion material)
2 N-type semiconductor (n type thermoelectrical conversion material)
3 Elevated-temperature side joined part
4 Low temperature side joined part
5 Elevated-temperature lateral electrode
6 and 7 Low-temperature lateral electrode
Q High temperature heat source
Th The elevated-temperature side temperature
Tc The low temperature side temperature
S Insulation space

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the high-temperature-exhaust-heat use power plant generated by a thermoelectric element using exhaust heat of various high temperature exhaust gases.
[0002]
[Description of the Prior Art]A high temperature exhaust gas is discharged from a solid oxide fuel cell (SOFC), an automobile engine, a gas engine, a gas turbine, a metal furnace, a ceramic kiln, a chemical industry furnace, and others. For example, the emission temperature of a metal furnace exit or a ceramic kiln exit is about 600 **, the SOFC operates at the elevated temperature of about 700-1000 **, and high temperature generates it. Although various proposals are made about those exhaust heat use, it is possible to generate electricity by a thermoelectric element as one of them.
[0003]A thermoelectric element is an element which transforms thermal energy into electric power directly using the thermo-electric effect (= Seebeck effect) which thermoelectromotive force generates among these both ends by giving a temperature gradient to the both ends of a thermoelectric element. The thermoelectrical conversion material with which two sorts of metal, different p-type semiconductor, n-type semiconductor, etc. are different is placed in parallel thermally, this element is electrically connected in series, load is connected outside, and a closed circuit comprises a thermoelectric element. Drawing 1 is a figure which illustrates a thermoelectric element theoretically, and shows the example which combined the p-type semiconductor and the n-type semiconductor as an example.
[0004]As for a p-type semiconductor and 2, the elevated-temperature side joined part and 4 are the low temperature side joined parts an n-type semiconductor and 3 one among drawing 1, Q shows a high temperature heat source, Th shows the elevated-temperature side

temperature, Tc shows the low temperature side temperature, and S is insulation space. The elevated-temperature lateral electrode 5 is formed in the elevated-temperature side joined part 3 in common, and the low-temperature lateral electrodes 6 and 7 are separately formed in the low temperature side joined part 4. In this thermoelectric element, if temperature-gradient deltaT=Th-Tc is given between the elevated-temperature side joined part 3 and the low temperature side joined part 4, voltage will occur between two electrodes (between 5 and 6, between 5 and 7). So, if load (R) is connected among the two electrodes 6 and 7 by the side of low temperature, current (I) can flow and it can take out as electric power (W).

[0005]The electric generating power W of such a thermoelectric element is expressed with a following formula (1). They are I:current, R:load resistance, S:thermoelectric power, deltaT=Th-Tc, r:internal resistance, and m=R/r among a formula (1) here. In the passage clear from a formula (1), it is greatly dependent on a temperature gradient (deltaT) with the elevated-temperature side temperature (Th) and the low temperature side temperature (Tc), and the electric generating power W is proportional to the square of deltaT. For this reason, electric generating power W of a thermoelectric element can be enlarged by enlarging the difference (deltaT) of the elevated-temperature side temperature (Th) and the low temperature side temperature (Tc). Since generation efficiency is also proportional to a temperature gradient (deltaT) mostly, generation efficiency can also make it high by enlarging.

[0006]

[Number 1]

$$W = I^2R = S^2\Delta T^2 \times \frac{m}{r\,(m+1)^2} \qquad (1)$$

[0007]For the purpose, the element which functions in a temperature requirement wide as a thermoelectric element is required. As a thermoelectrical conversion material which constitutes a thermoelectric element, conventionally, Intermetallic compounds, such as Bi_2Te_3, PbTe, $Si_{0.8}$germanium$_{0.2}$, and $FeSi_2$, are known, among these Bi_2Te_3 (BiTe system) is used as a common thermoelectrical conversion material. However, since these thermoelectrical conversion material is not an oxide but the thermoelectrical conversion material of non-oxide stock, There is not only a problem in respect of the performance in a pyrosphere, but even if it uses Bi_2Te_3, for example, there is a problem in respect of the endurance in a pyrosphere, such as not less than 250 **, and it is impractical above about 300 ** from the performance side.

[0008]In addition, about $Si_{0.8}$germanium$_{0.2}$, there is a track record as an object for the power generation in the universe as a thermoelectrical conversion material in a not less than 500 ** pyrosphere. However, at an elevated temperature, it is easy to sublimate this material and it needs a special protective construction, such as twisting doubly sublimation preventive

measures, for example, opaque quartz. Anyway, to be the thermoelectrical conversion material which can be equal to prolonged use is desired regardless of the conditions from ordinary temperature to an elevated temperature, atmosphere, etc. On the other hand, since $FeSi_2$ has the low performance as a thermoelectrical conversion material, it is not practical for the energy-recovery purpose.

[0009]As mentioned above, in the thermoelectrical conversion material known till the present, there is a problem in respect of the endurance in the pyrosphere of not less than 250 ** or not less than 300 **, and practicality has difficulty above about 300 ** also from the performance side. So, even if there was a hot exhaust gas source, it is made for the high temperature end of a thermoelectric generation device to be 300 ** or less, and it could not but generate electricity using the BiTe system.

[0010]From the above-mentioned viewpoint, this invention persons advance examination and research from the direction of many in some numbers paying attention to the thermoelectrical conversion material of oxide stock, and as part of that, A highly efficient oxide stock thermoelectrical conversion material which has the features, such as having the performance in which oxidation resistance is high and it is high in the wide temperature requirement ranging from the low temperature to an elevated temperature, is developed previously (JP,9-321346,A, JP,10-256612,A, JP,11-266038,A). Such materials have the high thermoelectrical transfer characteristic in the wide temperature requirement which ranges from liquid nitrogen temperature (-196 **) to not less than 800 **.

[0011]By the way, in a thermoelectric element, n type thermoelectrical conversion material is certainly required besides p type thermoelectrical conversion material. However, since each oxide material concerning the above-mentioned development is p type thermoelectrical conversion material, n type thermoelectrical conversion material is also wanted to be an oxide from fields, such as a coefficient of thermal expansion and junction nature. Although there are a $CdInO_4$ ($MgIn_2O_4$) system oxide (JP,7-291627,A) and a $Ba_{1-X}Sr_XPbO_3$ system oxide (JP,10-139543,A) as a n type oxide reported until now, These have some difficulties and it cannot necessarily be said as sufficient material. For example, since a $CdInO_4$ ($MgIn_2O_4$) system oxide contains Cd, it has a difficulty in respect of toxicity, and moreover, the thermoelectrical performance tends to fall at an elevated temperature. The $Ba_{1-X}Sr_XPbO_3$ system oxide contains Pb (lead) in basic structure, and there is a difficulty in respect of toxicity. And a main constitution element is three or more ingredients, and the oxide of these both systems has a demerit on material manufacture.

[0012]Although this invention persons looked for the thermoelectrical conversion material of n type oxide stock and were continuing various experiments and examination in view of the situation of the more than related with n type oxide stock thermoelectrical conversion material,

they were able to acquire some results. The n type oxide thermoelectrical conversion material which dopes a tetravalent element to basic oxide:In_2O_3 as an example has the performance which was excellent also in 800 ** or the elevated temperature beyond it as a thermoelectrical conversion material from ordinary temperature and ordinary temperature from low temperature which is called liquid-nitrogen-temperature-193 **, for example.

[0013]In addition to the above-mentioned result about In_2O_3 system material, further, The sintered compact of the mixture containing cobalt (Co) and carbon (C) (**: the alloy), When these sintered compacts were manufactured and the various characteristics were surveyed and pursued with these both ingredients paying attention to the sintered compact (**: the alloy) of the mixture containing sodium (Na), these sintered compacts found out having a power factor, others, and useful various characteristics as a n type thermoelectrical conversion material. In an ordinary temperature region, these have the characteristic also with a pyrosphere useful as a thermoelectrical conversion material, of course.

[0014]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the high-temperature-exhaust-heat use power plant which gives and generates a high temperature gradient (deltaT) as the high temperature side heat source using exhaust heat of various high temperature exhaust gases, using the thermoelectric element constituted using the above p type thermoelectrical conversion materials and the above specific n type thermoelectrical conversion materials.

[0015]

[Means for Solving the Problem]This invention is a high-temperature-exhaust-heat use power plant which forms a cooling-medium channel and a high temperature exhaust gas channel via a septum, and to a septum side by the side of a cooling-medium channel, or a septum side by the side of a high temperature exhaust gas channel One n type oxide thermoelectrical conversion material of following the (1) - (6), A thermoelectric element which connects p type thermoelectrical conversion material by turns is arranged, and a high-temperature-exhaust-heat use power plant which makes it the feature as it comes to take out electric power is provided.

(1) N type oxide thermoelectrical conversion material which is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject, and dopes at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3.

Make In_2O_3 into a subject and (2) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and Ir, N type oxide thermoelectrical conversion material which carries out annealing treatment in atmosphere which may return an oxide which doped at least one sort of tetravalent elements

chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3.
(3) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, N type oxide thermoelectrical conversion material which carries out annealing treatment in atmosphere which may return an oxide which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$. (However, A is at least one sort of elements chosen from Zr, Sn, and Ti among a formula, and it is x= 0.00005-0.1).
Make In_2O_3 into a subject and (4) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and Ir, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, N type oxide thermoelectrical conversion material calcinated in atmosphere which may return a raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn, Ti, Ce, V, Hf, Os, and Ir.
(5) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, N type oxide thermoelectrical conversion material calcinated in atmosphere which may return a raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn and Ti (however, the inside of a formula and A are at least one sort of elements chosen from Zr, Sn, and Ti, and are x= 0.00005-0.1).
(6) N type oxide thermoelectrical conversion material calcinated in atmosphere which is the n type oxide thermoelectrical conversion material which consists of In_2O_3, and may return material which generates In_2O_3 by In_2O_3 or calcination.
[0016]This invention is a high-temperature-exhaust-heat use power plant which forms a cooling-medium channel and a high temperature exhaust gas channel via a septum, and to a septum side by the side of a cooling-medium channel, or a septum side by the side of a high temperature exhaust gas channel One n type thermoelectrical conversion material of following the (1) - (6), A thermoelectric element which connects p type thermoelectrical conversion material by turns is arranged, and a high-temperature-exhaust-heat use power plant which makes it the feature as it comes to take out electric power is provided.
(1) N type thermoelectrical conversion material which consists of a sintered compact containing cobalt and carbon with a compound containing a compound, carbon, or carbon containing cobalt or cobalt which sinter a mixture.
(2) N type thermoelectrical conversion material which consists of a sintered compact which consists of cobalt and carbon.
(3) N type thermoelectrical conversion material which consists of an alloy which consists of

cobalt and carbon.
(4) N type thermoelectrical conversion material which consists of a sintered compact containing cobalt which sinters a mixture, carbon, and sodium of a compound containing cobalt or cobalt, a compound containing carbon or carbon, and a compound containing sodium.
(5) N type thermoelectrical conversion material which consists of a sintered compact which consists of cobalt, carbon, and sodium.
(6) N type thermoelectrical conversion material which consists of an alloy which consists of cobalt, carbon, and sodium.
[0017]
[Embodiment of the Invention]A high-temperature-exhaust-heat use power plant this invention is characterized by that comprises the following and which is generated using exhaust heat of various high temperature exhaust gases using a thermoelectric element.
Specific n type thermoelectrical conversion material.
P type thermoelectrical conversion material.
The thermoelectric element which consists of a specific n type thermoelectrical conversion material in this invention, and p type thermoelectrical conversion material, especially p type oxide thermoelectrical conversion material can be used at the not less than 300 ** elevated temperature which cannot use BiTe system materials, such as Bi_2Te_3.
[0018]SOFC is begun and a high temperature exhaust gas is discharged from the burning appliances (burner) in an automobile engine, the gas engine used with a cogeneration system, a gas turbine, etc., a blast furnace, a metal furnace, a fusion furnace, a ceramic kiln, the various furnaces in the chemical industry, etc. For example, although it changes with the kinds, scales, etc., the temperature of the exhaust gas of a metal furnace exit or a ceramic kiln exit is an elevated temperature which it says, for example is about 600 **, and the exhaust heat is followed on exhaust gas, and it is discharged. In this invention, it generates electricity using the thermoelectric element which used the heat (exhaust heat) of these high temperature exhaust gases, and was constituted using a specific n type thermoelectrical conversion material, and p type thermoelectrical conversion material, especially p type oxide thermoelectrical conversion material.
[0019]For example, although the operating temperature of SOFC is an elevated temperature of about 700-1000 **, and the temperature of an operation region changes with a fuel utilization rate and air utilization rates and there is a difference by a place, at the place which becomes an elevated temperature most, it becomes about 800-1000 **. If 20 ** air is used as a cooling medium, the temperature gradient of deltaT=780 - 980K can be taken at the maximum, and the big electric generating power W will be obtained. In SOFC, it can generate electricity by a thermoelectric element using the heat of the high temperature exhaust gas which is discharged from SOFC in addition to power generation by the SOFC itself. The same may be said of other

high temperature exhaust gases.

[0020]The power plant of this invention forms a cooling-medium channel and a high temperature exhaust gas channel via a septum (on namely, both sides of a septum), and arranges a thermoelectric element to the septum side by the side of a cooling-medium channel, or the septum side by the side of a high temperature exhaust gas channel. And a cooling medium is circulated to the cooling-medium channel, and a high temperature exhaust gas is made circulate and made to a high temperature exhaust gas channel. A septum may be formed tubular and may be formed in plate-like. When a septum is tubular, the inside of this pipe is made into a cooling-medium channel, the inside of this pipe is improved the outside of this pipe into a high temperature exhaust gas channel also as a high temperature exhaust gas channel, and it is good also considering the outside of this pipe as a cooling-medium channel. When a septum is plate-like, a side is made into a cooling-medium channel and while it is monotonous makes the another side side a high temperature exhaust gas channel. Fluids, such as gases, such as air, water, and an oil, are used as a cooling medium.

[0021]Although it is used as a component of a septum, selecting from a metallic material, a ceramics material, etc. suitably, an existing high temperature corrosion resistance material is preferred. If it is a metallic material, a heat resisting aluminum alloy, a heat-resistant titanium alloy, heat resistant cast iron, heat resisting steel (a ferrite series, a martensite system, austenite, etc.), Inconel, the Hastelloy alloy, etc. can be used, for example. If it is a ceramics material, alumina (aluminum$_2$O$_3$), silica (SiO_2), alumimium nitride (AlN), silicon nitride (Si_3N_4), zirconia (ZrO_2), silicon carbide (SiC), etc. can be used.

[0022]In the power plant of this invention, a fin is preferably provided in either a cooling-medium channel or a high temperature exhaust gas channel and its both. As a mode which provides a fin, one method of following the (1) - (4) can perform.

(1) A thermoelectric element is arranged in the septum side by the side of a cooling-medium channel, and provide the fin for collections of heat in the septum side by the side of a high temperature exhaust gas channel.

(2) While a thermoelectric element is arranged in the septum side by the side of a cooling-medium channel and providing the fin for collections of heat in the septum side by the side of a high temperature exhaust gas channel, provide the fin for heat dissipation in the cooling-medium channel side.

(3) A thermoelectric element is arranged in the septum side by the side of a high temperature exhaust gas channel, and provide the fin for heat dissipation in the septum side by the side of a cooling-medium channel.

(4) While a thermoelectric element is arranged in the septum side by the side of a high temperature exhaust gas channel and providing the fin for heat dissipation in the septum side by the side of a cooling-medium channel, provide the fin for collections of heat in the high

temperature exhaust gas channel side.
[0023]It is used selecting from a metallic material, a ceramics material, etc. as a component of a fin. An existing high temperature corrosion resistance material of especially the component of the collection-of-heat fin by the side of a high temperature exhaust gas channel is preferred. If it is a metallic material, steel and the chromium copper alloy which carried out nickel plating, SUS316, SUS310S, SUS317, Inconel, the Hastelloy alloy, etc. can be used. If it is a ceramics material, alumina (aluminum$_2O_3$), silica (SiO_2), alumimium nitride (AlN), silicon nitride (Si_3N_4), zirconia (ZrO_2), silicon carbide (SiC), etc. can be used.
[0024]In the case of SOFC or a gas turbine, since the heat exchanger is attached in those systems, efficient power generation is especially realizable by applying this invention to these heat exchangers. In SOFC, by a heat exchanger, carry out heat exchange of the fuel material, such as air for combustion by the exhaust gas and SOFC from a cell stack (supply air), or natural gas, and in a gas turbine. Usually, heat exchange is carried out for the supply air to the combustion gas and burner which are discharged through a turbine from a burner by a heat exchanger, and efficiency is raised. Since a temperature gradient high between exhaust gas and fuel material, such as a supply air and natural gas, exists in these heat exchangers, efficient power generation is realizable by applying this invention to these heat exchangers.
[0025]That is, in SOFC, although usually introduced at a room temperature, after it gives the heat of the exhaust gas of SOFC to this air or this fuel material and a supply air and fuel material carry out temperature up by a heat exchanger, they are supplied to a cell stack. In this case, by a heat exchanger, since the temperature of the exhaust gas from SOFC is an elevated temperature of about 400-900 **, since the big temperature gradient of hundreds of ** level exists between the air of a room temperature, or fuel material, this invention is applied to this heat exchanger.
[0026]In a gas turbine, the air for combustion is compressed by a compressor (for example, in the case of a micro gas turbine). After being heated by three to about 15 with a pressure ratio and being heated by the combustion gas from a turbine by a heat exchanger, it is mixed with fuel material, such as natural gas, and becomes gas of high temperature high pressure by combustion with a burner. Since a big temperature gradient exists in this heat exchanger between compressed air and the combustion gas (about 400-600 **) from a turbine, this invention is applied here.
[0027]Drawing 2 is a figure showing the example of a mode of the thermoelectric element used by this invention. The plurality of the p-n unit of a couple is connected with plate-like in series, two or more pairs of p type thermoelectrical conversion materials and n type thermoelectrical conversion material keep an interval, it is put side by side by turns, and ****** (each other is adjoined) p type thermoelectrical conversion material and n type thermoelectrical conversion material are connected in series by the electrode (connection split). It may connect alternately

with direct without an electrode (connection split). Although drawing 2 shows the case where 59 pairs of p-n units are connected as an example, a required number is connected and it generates electricity by giving temperature-gradient deltaT between the upper surface side and the undersurface side. The arrow (->) shows the flow of current among drawing 2.

[0028]If p type oxide thermoelectrical conversion material is used as a p type thermoelectrical conversion material when using n type oxide thermoelectrical conversion material by this invention, since both both are oxides, they are stable also at an elevated temperature and their production tops as a thermoelectric element are also dramatically advantageous. Since a coefficient of thermal expansion and other physical properties are also approximated especially, using ordinary temperature, an elevated temperature, and the big temperature gradient especially not less than 300 ** between elevated temperatures, it is efficient and electric power can be taken out. The production tops as a thermoelectric element are also advantageous.

[0029]As the p type thermoelectrical conversion material which constitutes the thermoelectric element of this invention, and a n type thermoelectrical conversion material, thermoelectrical conversion material like following the (1) - (17) developed by this invention person etc. can be used. (1) - (5) is p type oxide thermoelectrical conversion material, and (6) - (17) is n type thermoelectrical conversion material. These thermoelectrical conversion material has the effective thermoelectrical characteristic over a wide temperature requirement which it says is not less than 800 ** from ordinary temperature and ordinary temperature from liquid nitrogen temperature (-196 **).

[0030]<P type oxide thermoelectrical conversion material> (One) elementary composition type ACoxOy. The oxide thermoelectrical conversion material consisting of a substance expressed with (however, A is Li, Na, or K among a formula, x is 1<=x<=2, and y is 2<=y<=4), and the elementary composition type (A_ZB_{1-Z}) CoxOy Oxide thermoelectrical conversion material consisting of a substance expressed with [however, Li, Na or K, and B of A are Mg, Ca, Sr, Ba, Sc, Y, Bi, or Te among a formula, and 1<=x<=2 and y of z are 2<=y<=4 as for 0< z<1 and x] (JP,9-321346,A).

(2) Elementary composition type (A_ZB_{1-Z}) CoxOy [Li, Na or K, and B among a formula A However, Mg, Ca, Sr, Ba, Oxide thermoelectrical conversion material which is the oxide thermoelectrical conversion material which consists of a substance expressed with being Sc, Y, Bi, or Te and the range of z being 0< z<1, x being 1<=x<=2, and y being 2<=y<=4], and is characterized by including Mn, Fe, or Cu at Co site of these elementary composition type. Co site shows the position to which Co element exists in this oxide.

(3) Elementary composition type $Na(Co_ZA_{1-Z})_XO_Y$. (However, among a formula, 2<=y<=4 and z are 0< z<1, and x 1<=x<=2 and y) A -- Mn, Fe, or Cu -- it is -- the oxide thermoelectrical

conversion material consisting of a substance expressed. And elementary composition type $Na_PB_{1-P}(Co_ZA_{1-Z})_XO_Y$. Oxide thermoelectrical conversion material consisting of a substance expressed with (however, 0< p<1 and z of 2<=y<=4 and p are [x] 0< z<1 among a formula as for 1<=x<=2 and y, A is Mn, Fe, or Cu and B is Ca, Sr, Ba, Bi, or Y) (JP,10-256612,A).

(4) Elementary composition type $(Na_PB_{1-P})(Co_ZA_{1-Z})$ xOy [However, 0< p<=1 and z of x are 0< z<=1 among a formula (except for the case where both p and z are 1), and 1<=x<=2 and y 2<=y<=4 and p B, A, or B and A, Oxide thermoelectrical conversion material consisting of a substance expressed with, respectively, one sort or two sorts or more of elements chosen from Ag, Li, a lanthanoids, Ti, Mo, W, Zr, V, and Cr being shown] (JP,11-266038,A).

(5) Elementary composition type $(Na_PB_{1-P})(Co_ZA_{1-Z-q}Cu_q)$ xOy [However, x is 0< p<=1 among a formula, and 1<=x<=2 and y 2<=y<=4 and p z and q, Are 0< z<1, 0< q<1, and z<=1-q (except for the case where p is 1 and z is 1-q), and B, A, or B and A, Oxide thermoelectrical conversion material consisting of a substance expressed with, respectively, one sort or two sorts or more of elements chosen from Ag, Li, a lanthanoids, Ti, Mo, W, Zr, V, and Cr being shown] (JP,11-266038,A).

These (1) The p type oxide thermoelectrical conversion material of - (5) can be manufactured like the case where various oxides are manufactured.

[0031]< -- n type thermoelectrical conversion material: -- the 1(oxide)> -- it being the n type oxide thermoelectrical conversion material made into a subject, and (6) In_2O_3, N type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3, and is characterized by things. Especially the material that dopes at least one sort of elements chosen from Zr, Sn, and Ti among such tetrads has the outstanding thermoelectrical characteristic. This material "n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$[However, A is at least one sort of elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir among a formula, and it is x= 0.00005-0.1.] It can express ".

Make In_2O_3 into a subject and (7) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and Ir, N type oxide thermoelectrical conversion material which carries out annealing treatment in the atmosphere which may return the oxide which doped at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3, and is characterized by things.

(8) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, The n type oxide thermoelectrical conversion material

which carries out annealing treatment in the atmosphere which may return the oxide which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, and is characterized by things. (However, A is at least one sort of elements chosen from Zr, Sn, and Ti among a formula, and it is x= 0.00005-0.1).

Make In_2O_3 into a subject and (9) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and Ir, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, N type oxide thermoelectrical conversion material which calcinates in the atmosphere which may return the raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn, Ti, Ce, V, Hf, Os, and Ir, and is characterized by things.

(10) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, The n type oxide thermoelectrical conversion material which calcinates in the atmosphere which may return the raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn and Ti, and is characterized by things. (However, A is at least one sort of elements chosen from Zr, Sn, and Ti among a formula, and it is x= 0.00005-0.1).

(11) N type oxide thermoelectrical conversion material which calcinates in the atmosphere which is the n type oxide thermoelectrical conversion material which consists of In_2O_3, and may return the material which generates In_2O_3 by In_2O_3 or calcination, and is characterized by things.

[0032]The above (6) The n type oxide thermoelectrical conversion material of - (11) is applied to the application for patent 2000-244833 (filing date: August 11, Heisei 12, priority date : August 18, Heisei 11), and such materials can be manufactured like the case where various oxides are manufactured. That is, material which generates In_2O_3 by In_2O_3 or calcination, and material containing the element for a dope are used as a raw material, these are uniformly mixed as powder etc., and it is obtained by calcinating in gas atmospheres, such as air. Although calcination temperature in particular is not limited, it is preferred that it is the range of 900-1200 **. After mixing a raw material in this case, before calcinating, temporary quenching may be carried out in atmosphere, such as air.

[0033]This n type oxide thermoelectrical conversion material by heat-treating after calcination in the atmosphere which may be returned, That is, by carrying out annealing treatment (annealing) in the atmosphere which may be returned, the thermoelectrical performance, especially electrical resistivity can be improved further, and a power factor and a performance index can be further improved in connection with this. Although the temperature in particular of

annealing treatment is not limited, it is preferred that it is the range of 600-1150 **. For example, when a dope element is Ce, before the annealing treatment in the inside of the atmosphere which may be returned, the characteristic as the thermoelectric material does not have basic oxide In_2O_3 and an EQC, and it is almost equivalent, but. by carrying out annealing treatment in the atmosphere which may be returned, to basic oxide In_2O_3, the thermoelectrical performance as the thermoelectric material is markedly alike, and is improved. Calcination in the annealing treatment in the inside of the atmosphere which may be these-returned, or the atmosphere which may be returned is effective in an improvement of the performance about indium oxide (In_2O_3) itself.

[0034]Annealing treatment in the inside of the above-mentioned atmosphere which may return can be performed by placing this material into the furnace held, for example to the above high temperature, and circulating in a furnace the gas which may return. Especially if it is gas which may return this material as gas which may return, it will not be limited, but the gas which contains nitrogen or nitrogen preferably is used. The gas which may return is made to replace with circulating as mentioned above, and is good also as a sealing gas atmosphere. That is, this material may be placed into the atmosphere of the sealed gas which may return, such as a firing furnace, and this gas atmosphere may be held and processed to the above temperature. In addition, annealing treatment in the inside of the atmosphere which may be returned may be performed by placing and heat-treating this material all over a vacuum furnace.

[0035]After calcinating as mentioned above, it may replace with carrying out annealing treatment in the atmosphere which may be returned, and it may calcinate in the atmosphere which may be returned without passing through calcination in the atmosphere. In this case, it calcinates in the atmosphere which may return the raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from the material which generates In_2O_3 by In_2O_3 or calcination, Zr, Sn, Ti, Ce, V, Hf, Os, and Ir. In applying to indium oxide (In_2O_3) itself, it calcinates in the atmosphere which may return the material which generates In_2O_3 by In_2O_3 or calcination. Although this calcination temperature in particular is not limited, it is preferred that they are the temperature of the above-mentioned annealing treatment and the same temperature, i.e., the range of 600-1150 **.

[0036]Although the material which contains oxygen as the above "material which generates In_2O_3 by calcination" is used, Since In_2O_3 generates in this stage in carrying out temporary quenching in oxidizing atmospheres, such as air, before calcinating, the material which does not contain oxygen as that material can also be used. These elements of the material containing at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir are doped by In_2O_3 at the time of temporary quenching and calcination.

[0037]Also in this case, the n type oxide thermoelectrical conversion material, the EQC, or an almost equivalent n type oxide thermoelectrical conversion material produced by heat-treating in the atmosphere which may return the material after the above-mentioned calcination is obtained. Especially if it is gas which may return this material as gas which forms the atmosphere which may be returned, it will not be limited, but the gas which contains nitrogen or nitrogen preferably is used. Formation of the atmosphere by this gas is made to replace with gas circulating, and is good also as a sealing reducing gas atmosphere. It may carry out by placing and heat-treating this material all over a vacuum furnace as mentioned above also about the case where it calcinates in the atmosphere which may be returned without passing through heat treatment in this case, i.e., calcination.

[0038]If it is a raw material which can generate In_2O_3 by calcination as a raw material of In_2O_3, there will be no limitation in particular, and as the example, they are metal (In) and indium acid. [$In(OH)_3$, In_2O_3andxH_2O] Halogenides (InBr, $InCl_2$, $InBr_2$, InI_2, InF_3, $InBr_3$, etc.), a nitrate [$In(NO_3)_3$and3H_2O] **** is used. As a raw material of In_2O_3, the oxide (In_2O_3) itself may be used and a tetravalent element is doped by calcinating the raw material mixture which consists of material containing a tetravalent element. As a source of Zr doped to In_2O_3, they are metal (Zr), oxides (ZrO_2 etc.), and organic acid salt, for example. [$Zr(CH_3CO_2)_4$] A halogenide ($ZrCl_3$, $ZrCl_4$), oxy halogenides ($ZrOCl_2$, 8H_2O, etc.), etc. are used.

[0039]As a source of Sn, they are metal (Sn), an oxide (SnO_2), stannic acid (SnO_2andxH_2O), and hydroxide, for example. [$Sn(OH)_4$] Nitrate[$Sn(NO_3)_4$] Sulfate[$Sn(SO_4)_4$] Halogenides ($SnCl_4$, SnI_4, etc.) etc. are used. As a Ti source, they are metal (Ti), oxides (Ti_2O_3, TiO_2, etc.), and hydroxide, for example. [$Ti(OH)_3$] etc. Sulfate[$Ti(SO_4)_2$] Halogenides ($TiCl_4$, TiI_4, etc.) etc. are used. It will be used if it is a thing of a simple substance, an oxide, and the other forms that can be doped to In_2O_3 as other tetravalent sources of an element.

[0040]< -- n type thermoelectrical conversion material: -- the 2(non-oxide)> -- the n type thermoelectrical conversion material consisting of a sintered compact containing cobalt and carbon with the compound containing the compound, carbon, or carbon containing (12) cobalt or cobalt which sinter a mixture.

(13) N type thermoelectrical conversion material consisting of a sintered compact which consists of cobalt and carbon.

(14) N type thermoelectrical conversion material consisting of an alloy which consists of cobalt and carbon.

(15) N type thermoelectrical conversion material consisting of a sintered compact containing the cobalt which sinters a mixture, carbon, and sodium of the compound containing cobalt or

cobalt, the compound containing carbon or carbon, and the compound containing sodium.
(16) N type thermoelectrical conversion material consisting of a sintered compact which consists of cobalt, carbon, and sodium.
(17) N type thermoelectrical conversion material consisting of an alloy which consists of cobalt, carbon, and sodium.
[0041]The above (12) The n type thermoelectrical conversion material of - (17) is applied to the application for patent 2000-369331 (filing date: December 4, Heisei 12), and can be manufactured like the case where various carbide or an alloy is manufactured. That is, material containing cobalt, material containing carbon, material containing both the elements of cobalt and carbon, and material which contains sodium further are used as a raw material, these are chosen according to the target presentation, and it mixes uniformly as powder etc., and is manufactured by sintering the mixture (sintering). As a sintered atmosphere (synthetic atmosphere), although any of the reducing atmosphere of vacuum (decompression) atmosphere, atmospheric air, nitrogen, etc. may be sufficient, it is preferably carried out by the vacuum atmosphere and reducing atmosphere. If it is the temperature which can sinter a raw material mixture as a sintering temperature (synthesizing temperature), there will be no limitation in particular, but it can be preferably considered as the range of about 900-1400 **. The synthetic method by hot pressing, discharge plasma sintering, or scorification may be applied to sintering. Especially scorification is cooled, after being applied to composition of the n type thermoelectrical conversion material of the above (14) and (17) and fusing the mixture of cobalt and carbon in the case of the n type thermoelectrical conversion material of (14). Although the melting temperature should just be not less than about 1495 **, it can be preferably made into the range of 1495-1600 **. The same may be said of the n type thermoelectrical conversion material of (17).
[0042]The compound which contains cobalt or cobalt as a material containing cobalt is used. As the example, it is everything but metal (Co), for example, oxides (CoO, Co_3O_4, etc.), oxygen acid salts ($CoCO_3$ etc.), and organic acid salt. [$Co(CH_3COO)_2$] etc. Halogenides ($CoCl_2$, CoI_2, etc.) are mentioned. The compound which contains carbon or carbon as a material containing carbon is used. As the example, the material which can generate carbon at the time of sintering besides amorphous carbon or graphite, for example, hydrocarbon of liquefied or a solid state, higher alcohol, higher fatty acid, etc. are mentioned. As a material containing sodium, sodium compounds, such as sodium carbonate and sodium acetate, are mentioned, for example. $NaCo_XO_Y$ which is the material which contains cobalt and sodium especially (however, 1<=x<=2 and y of x are 2<=y<=4 among a formula.) setting formally below -- it is the same -- since what is necessary is just to add the material which contains carbon or carbon in this if it uses, it is advantageous also in respect of reservation of the

homogeneity of cobalt and carbon, etc. on a manufacturing process. Although the $NaCo_XO_Y$ itself is p type thermoelectrical conversion material, it is changed into n type thermoelectrical conversion material by making carbon contain. Conditions, such as a sintered atmosphere and sintering temperature, are the same as the above-mentioned case.

[0043]Since the n type thermoelectrical conversion material used by this invention has few main constitution elements, it is easy to manufacture it, and its manufacturing merit of the material itself is also large. The aforementioned <n-type thermoelectrical conversion material: In the n type oxide thermoelectrical conversion material of the 1(oxide)>, when a dope element is Zr, Ti, or both elements, composing elements are In and oxygen, and Zr, Ti or both elements, and since the toxic element is not included, it is safe. When the dope element is Zr, Sn, and Ti, it is comparatively cheap from a rare element, the precious metals, etc. not being included, and the merit on industrial use is dramatically large.

[0044]Thermoelectrical conversion material has a good way with high (large) Seebeck coefficient alpha (absolute number), the low (small) way of the electrical resistivity rho is good, the low (small) way of the thermal conductivity lambda is good, and the high (large) way of a power factor (PF) and the performance index Z is good. Among these, PF is calculated from alpha and rho as follows (2), and Z is calculated from alpha, rho, and lambda as follows (3). The above (6) The thermoelectrical conversion material of - (17) has the useful characteristic about those all.

[0045]

[Number 2]

$$PF = \frac{\alpha^2}{\rho} \qquad (2)$$

$$Z = \frac{\alpha^2}{\rho\lambda} \qquad (3)$$

[0046]Especially n type oxide thermoelectrical conversion material of aforementioned (6) - (11) is provided with the effective thermoelectrical performance from low temperature, such as liquid nitrogen temperature (-196 **), in a temperature requirement as wide as not less than 800 **. At temperature of not less than 800 **, the thermoelectrical performance does not fall from ordinary temperature, but it curves and it rises as temperature becomes high.

[0047]Drawing 3 - 5 are examples of said n type oxide thermoelectrical conversion material. It is a figure showing the thermoelectrical characteristic about [$(In_{0.995}Ti_{0.005})_2O_3$ (nitrogen annealing article)]. As drawing 3, an Seebeck coefficient of n type oxide thermoelectrical conversion material shows a value of -10x10 $^{-6}$ (V/K) by 80K, becomes large with a rise in heat henceforth, and has an effective value in a wide temperature requirement or more covering 700K. [It is because it is a n type that numerals of an Seebeck coefficient are - (minus) in

addition.] .About a power factor, 80K shows a value of 25×10^{-6} (W/mK^2), and it becomes large with a rise in heat henceforth, and has an effective value in a wide temperature requirement or more covering 700K. A power factor of n type oxide thermoelectrical conversion material shows an outstanding value called 230×10^{-6} (W/mK^2) at 780 ** (1053K) as drawing 4. A value outstanding almost like [performance index] a case of a power factor is shown as drawing 5.
[0048]Drawing 6 is an example of said p type oxide thermoelectrical conversion material. It is a figure showing the thermoelectrical characteristic about [$Na_{1.6}Co_2O_4$ (burned product)]. As drawing 6, a ZEBEKKU coefficient of p type oxide thermoelectrical conversion material shows a value of 50×10^{-6} (V/K) by 80K (-193 **), becomes large with a rise in heat henceforth, and has an effective value in a wide temperature requirement or more covering 700K. Although 80K shows a value of 570×10^{-6} (W/mK^2) about a power factor and there is a certain amount of up-and-down change with a rise in heat henceforth, it has an effective value in a wide temperature requirement or more covering 700K. Drawing 7 is the above-mentioned p type oxide thermoelectrical conversion material. [$Na_{1.6}Co_2O_4$ (burned product)] It is a figure showing the thermoelectrical characteristic of material (burned product of what doped Ag, La, Ce, etc. to $NaCo_2O_4$) of a same system. A performance index of p type oxide thermoelectrical conversion material becomes large with an ordinary temperature region to a rise in heat, and has the useful characteristic. For example, 740 ** (1013K) shows a value called 400×10^{-6} (/K) what doped Ag. Although there are some which become small to $NaCo_2O_4$ about a performance index according to a kind of dope element, other characteristics are taken into consideration, and it is selected and used.
[0049]
[Example]Hereafter, although this invention is explained in more detail based on an example, of course, this invention is not limited to these examples. In Examples 1-6, the thermoelectric element constituted using p type oxide thermoelectrical conversion material and said specific n type thermoelectrical conversion material as a thermoelectric element is used.
[0050]<<Example 1>> Drawing 8 - 10 are the figures showing this example. In the case where the septum of this example, i.e., the septum between a cooling-medium channel and a high temperature exhaust gas channel, is tubular, drawing 8 (a) is drawing of longitudinal section, and drawing 8 (b) is a cross-sectional view. A cooling-medium channel is provided inside a tubular partition, a high temperature exhaust gas channel is provided outside, and a thermoelectric element is arranged at the wall surface by the side of the cooling-medium channel of this septum. The graphic display is omitted although the lid etc. which the interval was kept in the periphery of this tubular partition, and the outer tube has been arranged (a high temperature exhaust gas channel is formed between this tubular partition and an outer tube),

and arranged the lead pipe for cooling-medium appropriation and high temperature exhaust gases on the upper and lower sides of these pipes are arranged.

[0051]Using p type oxide thermoelectrical conversion material and n type thermoelectrical conversion material, as the circular arrow of the left in drawing 2 shows, a thermoelectric element makes circular the plate-like thermoelectric element constituted like drawing 2, and arranges it to the inner surface of a tubular partition. By this, it can be simple and efficient, the heat of a high temperature exhaust gas can be used, and electric power can be taken out. As a modification of this example, a thermoelectric element may be arranged on the wall surface by the side of the high temperature exhaust gas channel of this septum, and a high temperature exhaust gas channel may be provided inside a tubular partition, and a cooling-medium channel may be provided outside. It is the same also in the example of the following which uses this point and a tubular partition.

[0052]Although a cooling-medium channel is provided inside a tubular partition and drawing 9 similarly provides a high temperature exhaust gas channel outside, it is an example which has arranged the thermoelectric element on the wall surface by the side of the high temperature exhaust gas channel of this septum, and has arranged the radiation fin to the cooling-medium channel, and has arranged the collection-of-heat fin to the high temperature exhaust gas channel. Drawing 9 (a) is drawing of longitudinal section, and drawing 9 (b) is a cross-sectional view. Thereby, the cold energy of a cooling medium can be effectively told to the low temperature side of a thermoelectric element, and the heat of a high temperature exhaust gas can be more effectively told to the elevated-temperature side of a thermoelectric element. As a modification of this example, one side may be arranged among a radiation fin and a collection-of-heat fin.

[0053]Although arrangement of a fin can be performed in various modes, drawing 10 is a figure showing some examples. When drawing 10 (a) keeps an interval up and down, and provides two or more fins in a circle and drawing 10 (b) provides a fin spirally, drawing 10 (c) is a case where a fin is provided in parallel with a tube axis. The heat of a high temperature exhaust gas is efficiently told to the elevated-temperature side of a thermoelectric element by these through a fin, and the cold energy of a cooling medium is efficiently told to the low temperature side of a thermoelectric element through a fin. Although these are examples arranged on the outside of a pipe, when arranging a fin inside a pipe, they can be arranged similarly.

[0054]<<Example 2>> When it constitutes a septum from a pipe, two or more pipes which have arranged the thermoelectric element in the wall or outer wall of this pipe may be put side by side. Drawing 11 is a figure showing the example, and is a case where two or more pipes (drawing 11 44 pieces) have been arranged to the cylindrical shell inside of the body. A cooling medium flows through the inside of a thermoelectric element, and a high temperature exhaust gas flows through the outside of a septum. In this case, the efficiency of heat transfer to a tube

wall side can be raised by arranging a collection-of-heat fin, the outside, i.e., the high temperature exhaust gas channel, of a septum. Drawing 12 is a figure showing the example. Two or more fins which kept the interval in the shellside up and down, and were provided in it in a circle in the example of drawing 12The flow of a high temperature exhaust gas can be bent by arranging so that [referring to drawing 10 (a)] may enter by turns, and efficiency of heat transfer can be raised further. In addition to the heat told directly from the tube wall surface, the heat of a high temperature exhaust gas is efficiently told to a thermoelectric element through a fin.

[0055]<<Example 3>> Drawing 13 is a figure showing other examples of this invention. A septum is constituted from a plate of a couple, an interval is kept, both boards are arranged, a cooling-medium channel is formed between them, and a high temperature exhaust gas channel is formed in the outside of each board. Drawing 13 (a) is a perspective view (four directions were cut and lacked), and drawing 13 (b) is an A-A line sectional view in drawing 13 (a). The statement of a fin is omitted in drawing 13 (a). The plate-like thermoelectric element constituted on the plate of the couple which has kept and arranged the interval, and which faces, i.e., each inside of each septum, like drawing 2 is arranged. In this way, a cooling-medium channel is constituted between both the arranged plate-like thermoelectric elements, and a high temperature exhaust gas channel is established in the outside of each plate.

[0056]Thereby, electric power can be taken out, using the heat of a high temperature exhaust gas simple and efficient. As a modification of this example, a thermoelectric element may be arranged on the outside of each plate, and a cooling-medium channel may be established for a high temperature exhaust gas channel in the outside of each board among both boards. It is the same also in the example of the following which uses this point and a tabular septum. The graphic display is omitted, although these monotonous four directions are closed by the heat-resistant member and the lead pipe for cooling-medium appropriation and high temperature exhaust gases is arranged on the upper and lower sides.

[0057]In this example, the heat of a high temperature exhaust gas and the cold energy of a cooling medium can be more effectively told to the elevated-temperature side of a thermoelectric element, the low temperature side, or its both by arranging a fin to a cooling-medium channel, a high temperature exhaust gas channel, or its both. Although the case where the fin has been arranged to the both is shown in drawing 13 (b), it may arrange to either. Although the mode of fin arrangement can be performed in various modes, drawing 14 is a figure showing the example. Drawing 14 (a) is a perspective view and the figure which drawing 14 (b) looked at from the front right among drawing 14 (a). As the graphic display, to the septum, the fin of a large number which have constant width keeps an interval in zigzag shape, and is arranged. That is, regular intervals are put on a transverse direction, it is arranged at a single tier, an interval is kept in the upper and lower sides, and it shifts like the

half of the fin width to the position of each fin in this sequence, and similarly two or more fins put regular intervals on a transverse direction, and are arranged at a single tier, and required sequence arrangement is carried out up and down in this way.

[0058]As it bends with the fin [directly under] of it further and goes to a transverse direction, after a high temperature exhaust gas's passing along the slit between ****** fins, and bending with the fin [directly under] of it, going to a transverse direction and passing along the slit of the same sequence, It goes caudad from the upper part, and progresses to zigzag shape, and the heat is told to the elevated-temperature side of a thermoelectric element through a fin in the meantime. The drawing 14 (b) middle point line shows the flow of such a high temperature exhaust gas. Although each fin of the illustration to drawing 14 is flat-surface quadrangular shape, with this, it may not be restricted but may be made into the shape of a strip of paper, and other proper shape. When it can fully let heat pass, it may be made for the direction of a high temperature exhaust gas style to become a fin and parallel.

[0059]Immobilization of the fin to a septum side can be performed by proper techniques, such as being based on welding or a bonding agent. When arranging a fin to the thermoelectric element side side, it may fix to whether to be direct via a bonding agent etc. in a thermoelectric element side, but it may fix to a thermoelectric element side via a septum at this. This septum is a septum for fin immobilization in a thermoelectric element side, and is not a septum for forming a cooling-medium channel and a high temperature exhaust gas channel in both sides. The designation of the septum for the fin immobilization concerned is carried out to the fin bottom plate at said drawing 9 and the following. Junction nature can also be raised between the fin bottom plate which provided thermal junction on a thermoelectric element and a fin in the thermoelectric element side as a method of keeping it good, and a thermoelectric element, being able to apply load. Drawing 15 is a figure showing an example of the load method using a spring. As drawing 15, the load means consists of a threaded rod, a presser-foot board, a spring, etc., and the junction can be kept good by pressing via a spring from the upper and lower sides. Here, in order to make thermal junction nature still better, the existing metallic foil of platinum (Pt) and oxidation resistance can also be inserted between a fin bottom plate and a thermoelectric element.

[0060]<<Example 4>> Drawing 16 is a figure (perspective view) showing other examples of this invention. At the point which constitutes a septum from a plate of a couple, although it is the same as that of Example 3 (drawing 13), it is the example which formed the pipe in the plate and made the inside of this pipe the high temperature exhaust gas channel. Each plate is made that much thick. A thermoelectric element is arranged inside each plate and between the plates of both the board couple serves as a cooling-medium channel. In rectangular directions, many tubular high temperature exhaust gas channels are arranged in a plate to the cooling medium which flows into the upper part [Drawing 16] towards another side from a lower part

from one side, and from one end of each tubular passage, a high temperature exhaust gas is turned to the end of another side, and is circulated from the left to the right or to from the right to the left. A tubular high temperature exhaust gas channel is constituted from one pipe, and it may be made to make it wind by making it bend one by one at the left end and a right end. As long as it says a high temperature exhaust gas channel by drawing 16 in parallel to the flow direction of a cooling medium, it may be formed in a sliding direction. The graphic display is omitted, although these monotonous four directions are closed by the heat-resistant member and the lead pipe for high temperature exhaust gases is arranged on the lead pipe of cooling-medium appropriation, and right and left by the upper and lower sides.As a modification of this example, between the plates of a couple serves as a high temperature exhaust gas channel in this case well also as a cooling-medium channel in the inside of this pipe in monotonous.

[0061]<<Example 5>> In SOFC, although usually introduced at a room temperature, after it gives the heat of the exhaust gas of SOFC to this air and a supply air carries out temperature up by a heat exchanger, it is supplied to a cell stack. In this case, since the temperature of the exhaust gas of SOFC is an elevated temperature of about 400-900 **, in a heat exchanger, the big temperature gradient of hundreds of ** level exists between the air of a room temperature. Drawing 17 (a) is a figure showing the example, in this example, it has two steps of air heat exchangers 1, and the air heat exchanger 2, and the catalyzed combustion room is arranged in the meantime. Since transfer of heat is performed via the septum between airstream and emission, both heat exchangers arrange a thermoelectric element to either septum side of an airstream side and the emission side (it is equivalent to said cooling-medium style side) (it is equivalent to said high temperature exhaust gas channel side). Drawing 17 (b) is an example which has arranged the thermoelectric element to the airstream side in the air heat exchanger 2. the heat exchanger used -- as tubular and plate-like and plate-like modification -- a section -- since wavelike or there are various forms, such as section zigzag shape, a thermoelectric element is arranged at the wall surface according to the shape of the septum.

[0062]<<Example 6>> In a gas turbine, the air for combustion, After being compressed by a compressor (it is three to about 15 at a pressure ratio in the case of a micro gas turbine) and being heated by the combustion gas from a turbine by a heat exchanger, it is mixed with fuel material, such as natural gas, and becomes gas of high temperature high pressure by combustion with a burner. Drawing 18 (a) is a figure showing the example. In a heat exchanger, a big temperature gradient exists between compressed air and the combustion gas from a turbine. As an example of the system, a combustion gas goes into a heat exchanger at about 600 **, and falls to about 300 ** by heat exchange with compressed air. Since transfer of heat is performed via the septum between airstream and a combustion-gas style in a heat exchanger, a thermoelectric element is arranged to either septum side of an airstream side and the combustion-gas style side (it is equivalent to said cooling-medium channel side) (it is

equivalent to said high temperature exhaust gas channel side). Drawing 18 (b) is an example which has arranged the thermoelectric element to the combustion-gas style side. the heat exchanger used -- as tubular and plate-like and plate-like modification -- a section -- since wavelike or there are various forms, such as section zigzag shape, a thermoelectric element is arranged at the wall surface according to the shape of the septum.

[0063]<<Example 7>> Drawing 19 is a figure showing the example of the thermoelectric element module used by this invention. $_2O_3$ was used as a n type thermoelectrical conversion material ($In_{0.995}Ti_{0.005}$), using $Na_{1.6}Co_2O_4$ as a p type oxide thermoelectrical conversion material. Platinum was used for the electrode and alumina was used for the electric insulating plate. Each coefficient of thermal expansion (beta) of these materials is an 8×10^{-6}/K grade. For this reason, the endurance in which electrode jointing was excellent to the thermal excursion is obtained. As shown in drawing 2, required-number connection of this unit is carried out, and it is arranged at a wall surface. Modular shape can be constituted in curved surface shape etc. according to a use.

[0064]

[Effect of the Invention]In this invention, p type thermoelectrical conversion material and a specific n type thermoelectrical conversion material are used as a component of a thermoelectric element.

Therefore, a high temperature exhaust gas is made into a heat source, and a big temperature gradient is given among cooling media, such as air, and using this, it is simple and efficient and can generate electricity.

By using exhaust heat of SOFC as a high temperature exhaust gas, 680K or more temperature gradients can be given among cooling media, such as air, and it can generate electricity simple and efficient together with power generation by the SOFC itself.

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1]It is a high-temperature-exhaust-heat use power plant which forms a cooling-medium channel and a high temperature exhaust gas channel via a septum, A high-temperature-exhaust-heat use power plant which makes it the feature as a thermoelectric element which connects one n type oxide thermoelectrical conversion material of following the (1) - (6) and p type thermoelectrical conversion material with a septum side by the side of a cooling-medium channel or a septum side by the side of a high temperature exhaust gas channel by turns is arranged and it comes to take out electric power.
(1) N type oxide thermoelectrical conversion material which is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject, and dopes at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3.
Make In_2O_3 into a subject and (2) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and Ir, N type oxide thermoelectrical conversion material which carries out annealing treatment in atmosphere which may return an oxide which doped at least one sort of tetravalent elements chosen from Zr, Sn, Ti, Ce, V, Hf, Os, and Ir to basic oxide In_2O_3.
(3) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, N type oxide thermoelectrical conversion material which carries out annealing treatment in atmosphere which may return an oxide which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$. (However, A is at least one sort of elements chosen from Zr, Sn, and Ti among a formula, and it is x= 0.00005-0.1).
Make In_2O_3 into a subject and (4) Zr, Sn, Ti, It is the n type oxide thermoelectrical conversion material which dopes at least one sort of tetravalent elements chosen from Ce, V, Hf, Os, and

Ir, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, N type oxide thermoelectrical conversion material calcinated in atmosphere which may return a raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn, Ti, Ce, V, Hf, Os, and Ir.

(5) It is the n type oxide thermoelectrical conversion material which makes In_2O_3 a subject and is expressed with formula $(In_{1-X}A_X)_2O_3$, Material and Zr which generate In_2O_3 by In_2O_3 or calcination, N type oxide thermoelectrical conversion material calcinated in atmosphere which may return a raw material mixture which consists of material containing at least one sort of tetravalent elements chosen from Sn and Ti (however, the inside of a formula and A are at least one sort of elements chosen from Zr, Sn, and Ti, and are x= 0.00005-0.1).

(6) N type oxide thermoelectrical conversion material calcinated in atmosphere which is the n type oxide thermoelectrical conversion material which consists of In_2O_3, and may return material which generates In_2O_3 by In_2O_3 or calcination.

[Claim 2]It is a high-temperature-exhaust-heat use power plant which forms a cooling-medium channel and a high temperature exhaust gas channel via a septum, A high-temperature-exhaust-heat use power plant which makes it the feature as a thermoelectric element which connects one n type thermoelectrical conversion material of following the (1) - (6) and p type thermoelectrical conversion material with a septum side by the side of a cooling-medium channel or a septum side by the side of a high temperature exhaust gas channel by turns is arranged and it comes to take out electric power.

(1) N type thermoelectrical conversion material which consists of a sintered compact containing cobalt and carbon with a compound containing a compound, carbon, or carbon containing cobalt or cobalt which sinter a mixture.

(2) N type thermoelectrical conversion material which consists of a sintered compact which consists of cobalt and carbon.

(3) N type thermoelectrical conversion material which consists of an alloy which consists of cobalt and carbon.

N type thermoelectrical conversion material which consists of a sintered compact containing cobalt which sinters a mixture, carbon, and sodium with a compound, comprising:

(4) A compound containing cobalt or cobalt.

A compound containing carbon or carbon.

Sodium.

(5) N type thermoelectrical conversion material which consists of a sintered compact which consists of cobalt, carbon, and sodium.

(6) N type thermoelectrical conversion material which consists of an alloy which consists of

cobalt, carbon, and sodium.

[Claim 3]The high-temperature-exhaust-heat use power plant according to claim 1 or 2, wherein said p type thermoelectrical conversion material is one p type oxide thermoelectrical conversion material of following the (1) - (5).

(1) Oxide thermoelectrical conversion material which consists of a substance expressed with the elementary composition type ACoxOy (A is Li, Na, or K among a formula, x is 1<=x<=2, and y is 2<=y<=4), or the elementary composition type $(A_Z B_{1-Z})$ CoxOy Oxide thermoelectrical conversion material which consists of a substance expressed with [Li, Na or K, and B of A are Mg, Ca, Sr, Ba, Sc, Y, Bi, or Te among a formula, and 1<=x<=2 and y of z are 2<=y<=4 as for 0< z<1 and x].

(2) The elementary composition type $(A_Z B_{1-Z})$ CoxOy [Li, Na or K, and B among a formula A Mg, Ca, Sr, Ba, Sc, Oxide thermoelectrical conversion material which is the oxide thermoelectrical conversion material which consists of a substance expressed with being Y, Bi, or Te and a range of z being 0< z<1, x being 1<=x<=2, and y being 2<=y<=4], and contains Mn, Fe, or Cu at Co site of these elementary composition type.

(3) Elementary composition type $Na(Co_Z A_{1-Z})_X O_Y$ (among a formula) as for 1<=x<=2 and y, 2<=y<=4 and z of x are 0< z<1 -- A -- Mn, Fe, or Cu -- it is -- oxide thermoelectrical conversion material which consists of a substance expressed. Or elementary composition type $Na_P B_{1-P} (Co_Z A_{1-Z})_X O_Y$ (among a formula) as for 1<=x<=2 and y, 0< p<1 and z of 2<=y<=4 and p are [x] 0< z<1, and A is Mn, Fe, or Cu -- B -- Ca, Sr, Ba, Bi, or Y -- it is -- oxide thermoelectrical conversion material which consists of a substance expressed.

(4) The elementary composition type $(Na_P B_{1-P})$ $(Co_Z A_{1-Z})$ xOy [0< p<=1 and z of x are 0< z<=1 among a formula (except for a case where both p and z are 1), and 1<=x<=2 and y 2<=y<=4 and p B, A, or B and A, Oxide thermoelectrical conversion material which consists of a substance expressed with, respectively, one sort or two sorts or more of elements chosen from Ag, Li, a lanthanoids, Ti, Mo, W, Zr, V, and Cr being shown].

(5) The elementary composition type $(Na_P B_{1-P})$ $(Co_Z A_{1-Z-q} Cu_q)$ xOy [x is 0< p<=1 among a formula, and 1<=x<=2 and y 2<=y<=4 and p z and q, Are 0< z<1, 0< q<1, and z<=1-q (except for a case where p is 1 and z is 1-q), and B, A, or B and A, Oxide thermoelectrical conversion material which consists of a substance expressed with, respectively, one sort or two sorts or more of elements chosen from Ag, Li, a lanthanoids, Ti, Mo, W, Zr, V, and Cr being shown].

[Claim 4]A high-temperature-exhaust-heat use power plant which a thermoelectric element is arranged in a septum side by the side of a cooling-medium channel, and provides a fin for collections of heat in a septum side by the side of a high temperature exhaust gas channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 3, and

is characterized by things.
[Claim 5]While a thermoelectric element is arranged in a septum side by the side of a cooling-medium channel and providing a fin for collections of heat in a septum side by the side of a high temperature exhaust gas channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 3, A high-temperature-exhaust-heat use power plant which provides a fin for heat dissipation in the cooling-medium channel side, and is characterized by things.
[Claim 6]A high-temperature-exhaust-heat use power plant which a thermoelectric element is arranged in a septum side by the side of a high temperature exhaust gas channel, and provides a fin for heat dissipation in a septum side by the side of a cooling-medium channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 3, and is characterized by things.
[Claim 7]While a thermoelectric element is arranged in a septum side by the side of a high temperature exhaust gas channel and providing a fin for heat dissipation in a septum side by the side of a cooling-medium channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 3, A high-temperature-exhaust-heat use power plant which provides a fin for collections of heat in the high temperature exhaust gas channel side, and is characterized by things.
[Claim 8]A high-temperature-exhaust-heat use power plant characterized by said high temperature exhaust gas being a not less than 300 ** high temperature exhaust gas in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 7.
[Claim 9]In the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 8, said high temperature exhaust gas, A high-temperature-exhaust-heat use power plant being a combustion gas of industrial furnaces, such as a gas engine in exhaust gas of a solid oxide fuel cell, and a cogeneration system or a combustion gas of a gas turbine, exhaust gas of an automobile engine or a fusion furnace, a ceramic kiln, and a heat treating furnace.
[Claim 10]A high-temperature-exhaust-heat use power plant which arranges to a septum side in a heat exchanger with air or fuel which supplies said thermoelectric element to a high temperature exhaust gas and this fuel cell from this fuel cell attached to a solid oxide fuel cell in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 8, and is characterized by things.
[Claim 11]A high-temperature-exhaust-heat use power plant which arranges said thermoelectric element in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 8 to a septum side in a heat exchanger of a combustion gas from this gas turbine attached to a gas turbine, and air supplied to this gas turbine, and is characterized by things.
[Claim 12]. [whether the outside of this pipe is made into a high temperature exhaust gas

channel by said septum being tubular and making the inside of this pipe into a cooling-medium channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 11, and] Or a high-temperature-exhaust-heat use power plant making the inside of this pipe into a high temperature exhaust gas channel, and becoming considering the outside of this pipe as a cooling-medium channel.

[Claim 13]A high-temperature-exhaust-heat use power plant characterized by said septum being plate-like in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 11.

[Claim 14]A high-temperature-exhaust-heat use power plant forming a pipe in said plate-like septum, and becoming in the high-temperature-exhaust-heat use power plant according to claim 13 considering inside of this pipe as a cooling-medium channel or a high temperature exhaust gas channel.

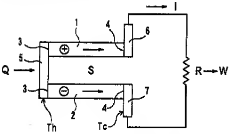
[Claim 15]A high-temperature-exhaust-heat use power plant, wherein a cooling medium which circulates said cooling-medium channel in the high-temperature-exhaust-heat use power plant according to any one of claims 1 to 14 is air.

[Translation done.]

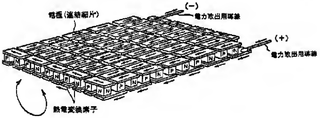
* NOTICES *

DRAWINGS

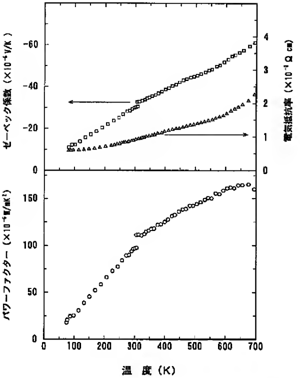
[Drawing 1]



[Drawing 2]



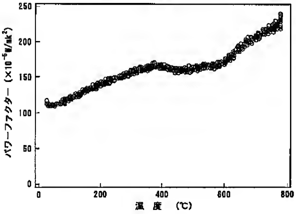
[Drawing 3]



($In_{0.995}Tl_{0.005})_2O_3$(窒素アニール品)の熱電特性

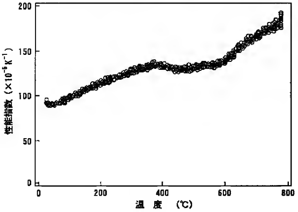
[Drawing 4]

$(In_{0.995}Tl_{0.005})_2O_3$窒素アニール品のパワーファクターの温度依存性

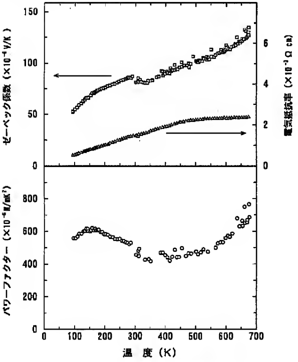


[Drawing 5]

(In$_{0.995}$Ti$_{0.005}$)$_2$O$_3$窒素アニール品の性能指数の温度依存性

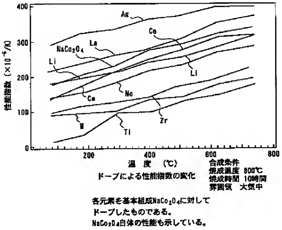


[Drawing 6]



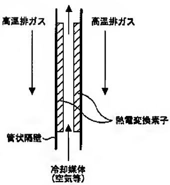
Na$_{1.6}$Co$_2$O$_4$（焼成品）の熱電特性

[Drawing 7]

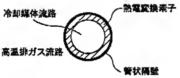


[Drawing 8]

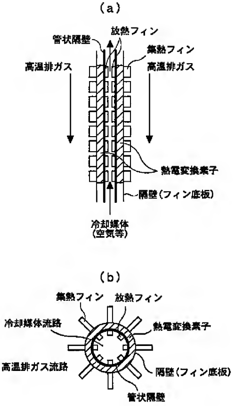
(a)



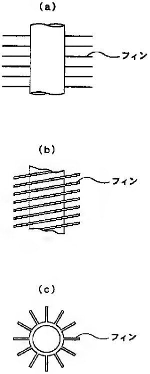
(b)



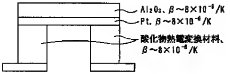
[Drawing 9]



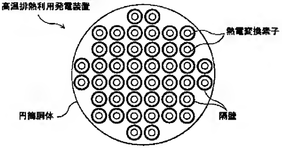
[Drawing 10]



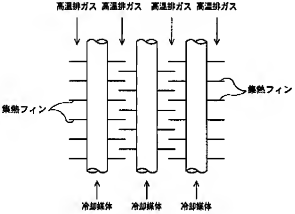
[Drawing 19]



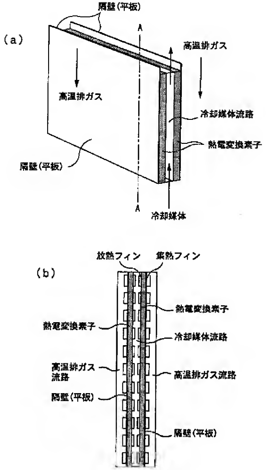
[Drawing 11]



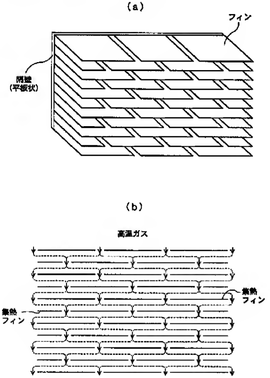
[Drawing 12]



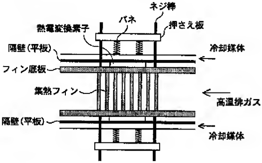
[Drawing 13]


(a)
隔壁(平板)
A
高温排ガス
高温排ガス
冷却媒体流路
熱電変換素子
隔壁(平板)
A
冷却媒体
(b)
放熱フィン
集熱フィン
熱電変換素子
熱電変換素子
冷却媒体流路
高温排ガス流路
高温排ガス流路
隔壁(平板)
隔壁(平板)

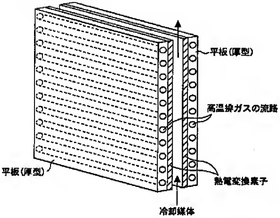
[Drawing 14]


(a)
フィン
隔壁(平板状)
(b)
高温ガス
集熱フィン
集熱フィン

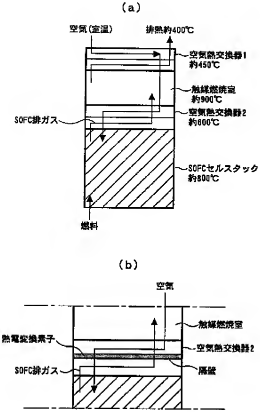
[Drawing 15]



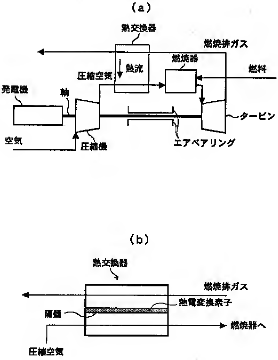
[Drawing 16]



[Drawing 17]


(a)
空気（室温）
排熱約400℃
空気熱交換器1
約450℃
触媒燃焼室
約900℃
SOFC排ガス
空気熱交換器2
約600℃
SOFCセルスタック
約800℃
燃料
(b)
空気
触媒燃焼室
熱電変換素子
空気熱交換器2
SOFC排ガス
隔壁

[Drawing 18]


(a)
熱交換器
燃焼排ガス
燃焼器
熱流
燃料
圧縮空気
発電機
軸
タービン
空気
圧縮機
エアベアリング
(b)
熱交換器
燃焼排ガス
熱電変換素子
隔壁
燃焼器へ
圧縮空気

[Translation done.]